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CERTIFICATION

I, the below named translator, hereby declare that: my name and post office address are as stated below; that I am knowledgeable in the English and German languages, and that I believe that the attached text is a true and complete translation of the German priority document bearing No. 102 35 255.0, filed with the German Patent Office on August 1, 2002.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Hollywood, Florida

Birgit Bartell

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Lerner & Greenberg, P.A.
P.O. Box 2480
Hollywood, FL 33022-2480
Tel.: (954) 925-1100
Fax.: (954) 925-1101

Description

Reflective mirror for lithographic exposure and production method

The invention relates to a method for producing a reflective mirror for the lithographic exposure of semiconductor products, there being formed on a substrate a multilayer structure and, above the latter, a capping layer made of a material on which a natural oxide layer forms in air. The invention furthermore relates to a reflective optical mirror according to the preamble of claim 9.

In semiconductor fabrication, the surfaces of semiconductor substrates or of layers arranged thereon are patterned lithographically by a photosensitive resist layer being deposited on them and exposed lithographically. During this lithographic exposure, a two-dimensional mask structure is imaged onto the resist layer. The carrier of the mask structure is a so-called reticle, here also called a mask. On this reticle, the structure to be exposed is realized in the form of an already patterned layer on an imaging scale magnified approximately 4 to 10 times. The pattern of this patterned layer is produced on the semiconductor substrate after having been reduced in size to the resist mask by means of an imaging optical arrangement. The exposed resist layer is developed and serves as a mask for an etching, an implantation or another treatment of the semiconductor substrate or of the layer to be patterned that is situated thereon.

Either transmission masks, whose structures are realized in a chromium layer, or reflection masks are used as a mask

(reticle) for the lithographic exposure of semiconductor products. Said reflection masks represent optical mirrors whose surfaces are covered with a patterning absorption layer. Reflection masks are used in particular for wavelengths in the extreme UV region, i.e. between 1 and 100 nm, since most materials absorb in this wavelength range. The reflection of the EUV wavelength (extreme ultraviolet) is achieved with the aid of multilayer structures composed of a multiplicity of thin layers or layer pairs at whose interfaces a fraction of the incident radiation is reflected in each case. Constructive interference of the radiation reflected at various interfaces produces a reflected beam which, in optically demagnified fashion, can be directed onto a semiconductor product, the mask structure arranged above the multilayer structure being imaged onto the resist layer of the semiconductor product.

A reflection mask of this type thus represents a reflective optical mirror. Above the multilayer structure, the mirror has a capping layer, which serves as a protective layer for the multilayer structure. The multilayer structure often comprises an alternate sequence of molybdenum layers and silicon layers. A silicon layer is then usually used as the capping layer, the silicon layer being arranged above the topmost molybdenum layer and having a larger layer thickness than the silicon layers of the multilayer structure. Typically, the layers of the multilayer structure have layer thicknesses of about 7 nm and the capping layer has a layer thickness of 10 to 20 nm. However, depending on the wavelength used, the layer thickness may deviate greatly from these particulars in order to effect a constructive interference of the reflected radiation at the relevant wavelength. A buffer layer is usually arranged above the capping layer, a patterned mask layer containing the structure being arranged on said buffer layer. The buffer layer is initially present over the whole area of the capping

layer as provisional protection thereof and is required in particular in the case of repairs to the mask structure of the patterned mask layer. Before the reflective optical mirror is used, the buffer layer is removed at the locations that are not covered by the patterned mask layer, so that the capping layer is uncovered there.

A natural oxide having a thickness of a few nanometers forms on a silicon surface of the capping layer that is exposed to air. This natural oxide growth arises spontaneously over the course of a few days to a few weeks and also continues over a relatively long time. Therefore, reflective optical mirrors occasionally have to be etched if they are used over a relatively long time, in order to remove the oxide layer that has formed. The oxide layer thickness to be removed must be determined precisely and the removal must be controlled precisely. Methods for doing this are not known, however.

The natural oxide growth on silicon surfaces in ambient air is subject to statistical fluctuations. The thickness of the oxide layer varies on different regions of a silicon surface. Therefore, the reflectivity, more precisely the reflection coefficient which represents the proportion of reflected radiation in relation to the incident radiation, is not homogeneous over the silicon surface.

The problem of inhomogeneous layer thicknesses of natural oxides could theoretically be combated through controlled etching-back of the oxide layers formed, but etching processes are also subject to statistical fluctuations, as a result of which the etching rate on the silicon oxide surface may be of varying magnitude locally.

Experiments are known in which the oxide growth was observed in water, in some instances also in hydrogen peroxide for different dopings. It is known, inter alia, to accelerate the oxide growth in hydrogen peroxide with the aid of platinum. Such experiments were carried out in order to investigate the time dependence of the oxide growth under different conditions.

The object of the present invention is to provide a reflective optical mirror having a reflectivity that is as homogeneous as possible over the mirror surface.

In the method mentioned in the introduction, this object is achieved by virtue of the fact that the capping layer is produced from a doped material and is brought into contact with hydrogen peroxide, as a result of which an artificially grown oxide layer is formed on the capping layer.

According to the invention, an oxide layer is produced artificially, which oxide layer covers the capping layer and therefore impairs the transparency of the mirror by a certain amount. Oxide layers are conventionally avoided for this reason. According to the invention, however, this oxide layer is produced by an accelerated growth process which results in the growth taking place homogeneously over the surface of the capping layer. The oxide layer thus formed has a homogeneity which is not achieved in the course of natural oxide growth, as a result of which better optical properties of the mirror are obtained overall. The disadvantage of the reduced transparency is compensated for over the course of time by the natural oxide growth which commences anyway. What is advantageous about the oxide layer formed according to the invention is that the further natural growth on the artificially grown oxide layer takes place at a comparatively

low growth rate, which means that inhomogeneities that possibly arise are formed much more weakly. According to the invention, unlike conventional practice, the capping layer is not produced from undoped material, but rather from a doped material. The latter is brought into contact with hydrogen peroxide, according to the invention, in order to grow a homogeneous oxide layer artificially. In particular it is provided that a catalyst, for example platinum, is added to the hydrogen peroxide, so that the artificially grown oxide layer is formed in the presence of the catalyst (platinum).

It is preferably provided that the capping layer is dipped into hydrogen peroxide having a concentration of between 10% and 50% for a time duration of between 3 and 120 minutes. It is precisely in the presence of platinum or another catalyst that an artificial oxide layer can grow within a short time, said layer only arising over the course of weeks or months under natural conditions.

It is preferably provided that the hydrogen peroxide is heated before and/or during the immersion of the capping layer. This makes it possible to achieve a further acceleration of the artificial oxide growth.

Preferably, a capping layer having a layer thickness of between 0.8 and 2.0 nm is produced through the contact with hydrogen peroxide. Even in the case of a subsequent natural oxide growth on this artificially produced oxide layer, it is ensured that a homogeneous layer is formed on the first 0.8 to 2.0 nm above the capping layer surface, where the oxide grows the fastest.

It is preferably provided that the concentration of the doping is chosen with a magnitude such that the natural oxide growth

on the oxide layer grown through contact with hydrogen peroxide is annually less than 10% of the layer thickness grown with the aid of hydrogen peroxide.

It is preferably provided that the capping layer is produced from an n-doped material. Although p-type dopings are also appropriate, in principle, for doping the capping layer, in order to achieve an accelerated oxide growth, it has been observed that the growth process is slowed down significantly precisely on n-doped capping layer material, in particular silicon.

In order to provide a sufficiently high and homogeneous doping over the entire surface of the reflective optical mirror, the capping layer is preferably applied to the multilayer structure by a deposition, for example by a chemical vapor deposition (CVD) or by a physical deposition (PVD; physical vapor deposition), for instance by sputtering. The negative doping is preferably introduced into the capping layer during this deposition by supplying the dopant together with the basic material of the capping layer to the surface of the reflective mirror. This in-situ doping has the advantage that there is no need for any subsequent process steps for doping the capping layer. As an alternative, however, the doping may subsequently be introduced into the capping layer by means of an implantation with a low implantation energy. Equally, it is conceivable for the initially undoped capping layer to be brought into contact with a dopant-containing medium, for instance a liquid or another fluid, so that the dopant can diffuse into the capping layer. During this treatment, the deeper layers of the multilayer structure are protected from attack by the dopant.

The capping layer is preferably produced from n-doped silicon. The growth of an amorphous silicon layer is preferred in this case.

The object on which the invention is based is furthermore achieved by means of a reflective optical mirror having
a substrate,
a multilayer structure, which reflects electromagnetic radiation through constructive interference, and
a capping layer above the multilayer structure,
the capping layer being composed of a material on which a natural oxide layer forms in air,
in which case, according to the invention, the material of the capping layer is doped with a doping and the oxide layer has a region having a layer thickness in which the same doping as the doping of the capping layer is incorporated into the oxide of the oxide layer.

The invention's reflective optical mirror for the lithographic exposure of semiconductor products has an oxide layer or a region of an oxide layer which corresponds to a minimum layer thickness and in which the same doping as the doping of the capping layer is incorporated into the oxide of the oxide layer. On the finished mirror, too, the identical doping indicates an oxide layer formed contemporaneously with the production of the capping layer; dopings or impurities which arise on account of changing ambient conditions and are of the kind that arise during natural oxide growth cannot occur in the artificially produced oxide. The oxide layer thus produced has a homogeneous layer thickness and thus improves the optical properties of the mirror.

The reflective mirror preferably has an oxide layer which has a layer thickness of between 0.8 and 2.0 nm. The capping layer

is preferably composed of n-doped silicon; phosphorus or arsenic is preferably provided as the doping. However, according to the invention, further customary n-conducting dopants can also be introduced into the capping layer of the reflective mirror for the purpose of ending the natural oxide growth. The silicon-containing capping layer is preferably amorphous.

In accordance with the intended purpose for the lithographic exposure of semiconductor products, the reflective mirror preferably has a patterned mask layer, whose structure can be transferred to one or more semiconductor products. A buffer layer may be situated between the patterned mask layer and the capping layer, but is removed on the regions of the capping layer which are not covered by the mask layer. The natural oxide forms at these uncovered locations.

The multilayer structure of the reflective mirror is preferably dimensioned such that electromagnetic radiation having a wavelength which is greater than 1 nm and less than 100 nm is reflected. In particular extremely short wavelengths of between 1 and 20 nm, for example 13 nm, which are far removed from the spectrum of conventionally used wavelengths in the UV region, can be used with the aid of the reflective mirror according to the invention with a high luminous efficiency for the lithographic patterning.

The invention is described below with reference to Figs. 1 to 8, in which:

Figs. 1 to 5 show a reflective optical mirror in cross-sectional view in different stages of the method according to the invention,

Fig. 6 shows the temporal profile of the natural oxide growth on a conventional reflective mirror,

Fig. 7 shows the temporal profile of the natural oxide growth in a reflective mirror according to the invention, and

Fig. 8 shows a simplified diagrammatic construction during the lithographic patterning of a semiconductor product with the aid of a reflective mirror.

Fig. 1 shows a reflective mirror comprising a substrate 10 and a sequence of thin layers 11a, 11b deposited one on top of the other. A semiconductor substrate or else any other sufficiently thick and stable substrate can be used as the substrate 10. The layer thicknesses of the individual layers 11a, 11b are dimensioned such that a wavelength λ is reflected at the interfaces of mutually adjacent layers in such a way that the reflected partial beams interfere constructively with one another; the highest possible light intensity of the overall reflected radiation is desirable for a short exposure time during the exposure of the semiconductor products. The large angle of incidence of electromagnetic radiation having the wavelength λ is shown if Fig. 1 merely in order to illustrate the reflection at different interfaces; in practice, the reflection takes place practically perpendicularly to the surface of the multilayer structure 11.

The layer sequence 11 in Fig. 1 is produced by progressive deposition of the individual layers, for example by means of a CVD process (preferably sputtering; ion beam deposition), in which the gas composition is varied with respect to time such that the gases supplied to the surface form the desired layer sequence. A two-layer structure comprising layers of alternate material composition is preferably formed, for instance a

sequence of molybdenum and silicon layers alternating with one another. The layer thickness of the individual layers depends on the wavelength used and follows from the condition of constructive interference of the reflected radiation.

In accordance with Fig. 2, a capping layer 12 is applied to the reflective mirror, in the case of which the inner structure of the multilayer structure 11 is no longer specifically illustrated, preferably by means of a chemical vapor deposition in which silicon and, at the same time, the dopant for the negative doping of the capping layer are deposited. Phosphorus or arsenic, for example, may be used as the dopant; all that is critical is that the concentration of the dopant is chosen to be high enough in order to obtain a suitable growth behavior of the oxide grown artificially with the aid of hydrogen peroxide. A high dopant concentration of n-type dopings, in particular, has the effect that - in particular during the growth of n-type silicon with the aid of hydrogen peroxide and platinum as catalyst - a very fast growth is achieved, but is slowed down greatly after a few hours. Although this does not necessarily equate to a saturation, the slowing down of the oxide growth obtained (during the accelerated growth process brought about artificially) is suitable for making it more difficult even for a subsequent natural oxide growth to occur. However, even in the case of p-type dopings and with other basic materials for the capping layer, an oxide layer thickness having a homogeneity which cannot be achieved during natural growth is obtained on account of the artificially accelerated growth.

Firstly a buffer layer 13 is applied to the capping layer 12 and a mask layer 14 is applied to said buffer layer, which mask layer is subsequently patterned, as illustrated in Fig. 3. The reflective mirror 1 thus acquires its mask structure

which prevents reflection of the radiation in the regions covered by the mask layer. In the EUV region, in particular, the absorption of the radiation in the mask layer leads to the formation of a positive mask on the reticle 1.

In accordance with Fig. 4, the buffer layer is removed in order to uncover the underlying, according to the invention heavily negatively doped capping layer made of silicon 12. If the patterning of the mask layer 14 is defective, defects can be corrected with the aid of conventional methods before the buffer layer 13 is removed where it is uncovered.

An oxide layer 15 forms on the uncovered silicon layer 12 which for the first time is exposed to the ambient air for a relatively long time, which oxide layer grows to form a layer thickness of a few nanometers.

The oxide growth brought about artificially is illustrated diagrammatically in Fig. 5. The optical mirror, immersed in an aqueous solution of hydrogen peroxide 20 at least with its capping layer 12, is oxidized at room temperature or at elevated temperature, preferably in the presence of platinum or another catalyst. The accelerated oxidation leads to a homogeneous growth which anticipates an inhomogeneous natural growth which otherwise takes place.

The temporal profile of the natural oxide growth of silicon and dioxide is illustrated diagrammatically and purely qualitatively in Fig. 6. It can be seen that the layer thickness of the oxide layer 15 rises monotonically and the time dependence of the oxide layer thickness does not exhibit any particularly striking features. This behavior is observed in the case of conventional capping layers made, for instance, of undoped silicon.

The growth in the case of a method according to the invention for producing a reflective optical mirror is illustrated in Fig. 7. Firstly, during a time t_s, which may lie between half an hour and 2 hours when using hydrogen peroxide with platinum at room temperature, a very much faster growth is obtained than in the case of natural oxidation. If the envisaged minimum layer thickness d_S of between 0.8 and 2.0 nm, for example, is reached, the artificial oxide growth is terminated. Although the optical mirror produced has an oxide layer which reduces the reflectivity of the mirror, this reduction is of the same intensity on all regions of the uncovered capping layer on account of the homogeneity of the artificial oxide, so that the mirror has better properties for the lithographic exposure of semiconductor products.

The time-dependent layer thickness profiles of Figs. 6 and 7 are not shown to scale; in particular, the time axis in Fig. 6 and Fig. 7 is not necessarily linear. However, Figs. 6 and 7 reveal that the artificially produced oxide is grown significantly faster than a natural oxide of comparable thickness. Primarily, a possible natural growth on the artificially produced oxide layer (in Fig. 7 the right-hand arm of the layer thickness function to the right of the break point at the time t_s) takes place at most with the same low growth rate as in the case of natural growth after reaching a corresponding total layer thickness, if not even with a reduced growth rate by comparison therewith.

With the aid of the capping layer doped according to the invention on the reflective mirror, a natural oxide layer is formed which has a homogeneous layer thickness over the entire surface of the capping layer. The layer thickness therefore remains homogeneous and practically constant for a long time.

This enables a homogenous reflectivity of the reflective mirror, which can be utilized, in particular in semiconductor fabrication, in order to reduce the exposure time for patterning semiconductor products and to increase the throughput.

Fig. 8 diagrammatically shows the construction of a device for the lithographic exposure of a semiconductor product 2 with the aid of a reflective optical mirror (reticle) 1. A radiation source 4 for electromagnetic radiation in the extreme UV region between 1 and 100 nm is directed at the reticle 1 by a first imaging optical arrangement (not illustrated) and generates, at the level of the mask layer 14, an intermediate image which is imaged onto the semiconductor product 2, in particular a wafer 2, after having been demagnified by a factor of 4 to 10 with the aid of a second imaging optical arrangement 3, which likewise operates in a reflective manner. With the aid of the exposure operation, a resist layer (not specifically illustrated) arranged on the semiconductor substrate is exposed with the demagnified structure of the mask layer 14 and can subsequently be developed in order to pattern a layer (not illustrated) on the semiconductor substrate 2. The stepper 5 moves the semiconductor substrate 2 stepwise in the x and y directions in order that different regions on the semiconductor wafer 2 can repeatedly be exposed one after the other. Since a large number of exposure operations are necessary and, moreover, a large number of semiconductor substrates 2 are repeatedly exposed many times in this way, the throughput in the fabrication of semiconductor circuits depends on the required exposure time. By virtue of the capping layer that is heavily negatively doped according to the invention on the reticle 1, a homogeneous oxide layer is formed in accordance with the saturation layer thickness. Since further oxide growth no

longer occurs to an appreciable extent, the reflectivity of the mirror remains very high and homogeneous, which enables shorter exposure operations.

Patent claims

1. A method for producing a reflective mirror (1) for the lithographic exposure of semiconductor products (2), there being formed on a substrate (10) a multilayer structure (11) and, above the latter, a capping layer (12) made of a material on which a natural oxide layer (15) forms in air, characterized in that the capping layer (12) is produced from a doped material and is brought into contact with hydrogen peroxide (20), as a result of which an artificially grown oxide layer (15) is formed on the capping layer (12).

2. The method as claimed in claim 1, characterized in that the capping layer is dipped into hydrogen peroxide (20) having a concentration of between 10% and 50% for a time duration of between 3 and 120 minutes.

3. The method as claimed in claim 1 or 2, characterized in that the hydrogen peroxide (20) is heated before and/or during the immersion of the capping layer (12).

4. The method as claimed in one of claims 1 to 3, characterized in that a capping layer (12) having a layer thickness (d_S) of between 0.8 and 2.0 nm is produced through the contact with hydrogen peroxide (20).

5. The method as claimed in one of claims 1 to 4, characterized in that the concentration of the doping (18) is chosen with a magnitude such that the natural oxide growth on the oxide

layer (15) grown with the aid of hydrogen peroxide (20) is annually less than 10% of the layer thickness (d_S) grown with the aid of hydrogen peroxide (20).

6. The method as claimed in one of claims 1 to 5, characterized in that the capping layer (12) is produced from an n-doped material.

7. The method as claimed in one of claims 1 to 6, characterized in that the capping layer (12) is applied by means of a deposition, and in that the n-type doping (12) is introduced into the capping layer (12) during the deposition.

8. The method as claimed in one of claims 1 to 7, characterized in that the capping layer (12) is produced from doped silicon.

9. A reflective optical mirror (1) for the lithographic exposure of semiconductor products (2), the mirror (1) having a substrate (10), a multilayer structure (11), which reflects electromagnetic radiation through constructive interference, and a capping layer (12) above the multilayer structure (11), the capping layer (12) being composed of a material on which a natural oxide layer (15) forms in air, characterized in that the material of the capping layer (12) is doped with a doping (18) and in that the oxide layer (15) has a region having a layer thickness (d_S) in which the same doping (18) as the doping (18) of the capping layer (12) is incorporated into the oxide of the oxide layer (15).

10. The reflective mirror as claimed in claim 9, characterized in that the oxide layer (15) has a layer thickness (d_s) of between 0.8 and 2.0 nm.

11. The reflective mirror as claimed in claim 9 or 10, characterized in that the capping layer (12) is composed of n-doped silicon.

12. The reflective mirror as claimed in one of claims 9 to 11, characterized in that the capping layer (12) is doped with phosphorus or arsenic.

13. The reflective mirror as claimed in one of claims 9 to 12, characterized in that the capping layer (12) is amorphous.

14. The reflective mirror as claimed in one of claims 9 to 3, characterized in that the mirror (1) has a patterned mask layer (14) for patterning a semiconductor product (2).

15. The reflective mirror as claimed in one of claims 9 to 14, characterized in that the patterned mask layer (14) is arranged above the capping layer (12).

16. The reflective mirror as claimed in one of claims 9 to 15, characterized in that the multilayer structure (11) is dimensioned such that electromagnetic radiation having a wavelength which is greater than 1 nm and less than 100 nm is reflected.

Abstract

Reflective mirror for lithographic exposure and production method

In a reflective optical mirror (1) for semiconductor fabrication with a capping layer (12) above a reflective multilayer sequence (11), according to the invention, a doping (18) is provided for the capping layer (12) and an artificial oxide layer (15) is grown on the capping layer (12) with the aid of hydrogen peroxide (20), in particular in the presence of a catalyst (Pt). The artificially grown oxide layer (15) is more homogeneous than a naturally grown oxide and thereby improves the optical properties of the mirror during the lithographic exposure of semiconductor products.

Fig. 5